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TITLE: ULTRAVIOLET-ABSORBING COLORLESS TRANSPARENT GLASS

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TOYO GLASS CO LTD N/A

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INT-CL (IPC): C03C004/08, C03C003/085

ABSTRACT:

PROBLEM TO BE SOLVED: To obtain the subject glass at lower cost more easily and more colorlessly than conventional ones.

SOLUTION: This glass is obtained by incorporating 0.02-0.07 wt.% of erbium oxide as color fading agent in a soda-lime glass containing 0.3-0.6 wt.% of cerium oxide and ≤0.05 wt.% of iron oxide. Incorporation of the cerium oxide affords this glass with ultraviolet light absorption effect. Yellowish color due to the iron oxide and cerium oxide can be corrected owing to the pale pinky color of the erbium oxide, getting virtually colorless. The color

development of the erbium oxide is highly stable, being hard to be influenced
by atmospheric change or an oxidizing agent such as the cerium oxide, thereby
easily affording desired effects.

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(54)【発明の名称】　紫外線吸収無色透明ガラス

(57)【要約】

【課題】　従来のものよりより安価で、より容易に、より無色に近い紫外線遮断無色透明ガラスを得る。

【解決手段】　重量%で酸化セリウム０．３～０．６%、酸化鉄０．０５%以下を含むソーダライムガラスで、消色剤として酸化エルビウム０．０２～０．０７%を添加する紫外線吸収無色透明ガラスである。酸化セリウムを加えることで紫外線吸収効果を得る。酸化鉄及び酸化セリウムで黄色味がかった色は酸化エルビウムの淡いピンク色で補正されて無色に近くなる。酸化エルビウムの発色はきわめて安定していて、雰囲気の変化や酸化セリウムのような酸化剤の影響を受けにくく、所望の効果を容易に得ることができる。

1

【特許請求の範囲】

【請求項1】　重量%で酸化セリウム0．3～0．6%、酸化鉄0．05%以下を含むソーダライムガラスで、消色剤として酸化エルビウム0．02～0．07%を添加したことを特徴とする紫外線吸収無色透明ガラス

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、特にガラスびんとして用いて好適な紫外線吸収無色透明ガラスに関する。

【0002】

【従来の技術】ガラスびんにおいては、内容物の変質を防ぐために紫外線を吸収し、しかも、内容物の様子を正確に確認することのできる無色透明性を有するものが望まれている。従来、このような用途のガラスは、特公昭45－17794号、特公平5－354号などで提案されている。前者のものは、ソーダライムガラスにセリウム酸化物を0．2～0．5重量%、ネオジウム酸化物を0．05～0．3重量%加えるというもので、セリウム酸化物を加えることで紫外線を吸収し、それによって黄色味をおびる色を消色剤であるネオジウム酸化物を加えることで無色に近くなるよに補正しようというものである。後者のものは、容器の最大長を250mm以下とし、重量%で0．04～0．1%の酸化セリウムと、0．065%以下の酸化鉄を含有させたソーダライムガラスのびんである，やはり、酸化セリウムを添加することで紫外線を吸収し、黄色味を助長させる酸化鉄の含有量を抑えると共にびんの最大長さを制限することでガラスが黄色に見えることを極力抑えようというものである。

【0003】

【発明が解決しようとする課題】上記の従来技術の前者のものは、青紫色を付けるネオジウム酸化物を加えることで、酸化セリウムの黄色若しくは黄緑色を消して無色*

2

*に近づけようとするものであるが、ネオジウム酸化物が高価であるうえに、添加する分量が難しく、少なすぎるとガラスは黄色ないしは黄緑色を呈し、多すぎると青色を呈してしまうという課題がある。

【0004】上記の従来技術の後者のものは、大型のびんが作れない上に、セリウムの添加量が少ないから十分な紫外線吸収効果を期待できず、また、セリウム酸化物による黄色味を消すことができないから、結局ガラスの色は無色とすることができず、黄色味をおびたガラスとなってしまう。

【0005】本発明は、このような課題を解決するもので、より安価で、より容易に、より無色に近い紫外線吸収無色透明ガラスを得ることができるものである。

【0006】

【課題を解決するための手段】本発明は、重量%で酸化セリウム0．3～0．6%、酸化鉄0．05%以下を含むソーダライムガラスで、消色剤として酸化エルビウム0．02～0．07%を添加したことを特徴とする紫外線吸収無色透明ガラスである。

【0007】本発明においては、酸化セリウムを加えることで紫外線吸収効果を得る。酸化セリウムの添加量は、少なすぎては紫外線吸収作用が弱く、多すぎてはガラスが強く発色し無色透明とすることができず、0．3～0．6%の量が双方の要素のバランスが良く、好適である。表1に酸化セリウムの添加率と紫外線吸収率の関係を示す，この表は、紫外線吸収率を該当波長範囲での平均吸収率と定義し算出した。すなわち、10nm毎の透過率を100から引いて、その平均値を求めている，このように、酸化セリウムの添加量を増やすと、紫外線吸収率が向上する，0．3～0．6%とすれば、実用的な紫外線吸収率を得ることができる。なお、表1におけるガラスの厚みは3mmである。

【表1】

ガラス厚み：3㎜　　単位：%

| 波長範囲 / 酸化セリウム添加率 | 310 ～ 350nm | 360 ～ 400nm | 310 ～ 400nm |
|---|---|---|---|
| 0（通常フリント） | 51．68 | 11．31 | 31．49 |
| 0．3% | 91．05 | 18．14 | 54．59 |
| 0．4% | 92．60 | 21．11 | 56．85 |
| 0．6% | 93．93 | 24．28 | 59．10 |

【0008】酸化セリウムを加えることで、ガラス中に不純物として存在している鉄を酸化する，そのため、2価の鉄イオンの緑色着色が少なくなり、3価の鉄イオンの黄色が多くなる，これにより、明度Yが大きくなり、主波長λdは長波長側へシフトし、ガラスの色が黄色味がかる。不純物である酸化鉄の含有量を0．05%以下※

※に抑えることで、ガラスの黄色ないし黄緑色の発色を最小限に抑制する，なお、酸化鉄の含有量を0．05%以下に抑えることは、当業者にとって容易になし得ることである，

【0009】酸化鉄の含有量を抑えるだけではガラスを無色にすることはできない。そこで、本発明において

3

は、消色剤として酸化エルビウム0．02～0．07%を添加する。酸化セリウムで黄色味がかった色は酸化エルビウムの淡いピンク色で補正されて無色に近くなる、酸化エルビウムの発色はきわめて安定していて、雰囲気の変化や酸化セリウムのような酸化剤の影響を受けにくく、所望の効果を容易に得ることができる。

【0010】

【実施例】本発明の実施例を表2に示す。酸化セリウムを0．3%、0．4%又は0．6%添加し、それぞれについて消色剤を添加したもの（実施例）と添加しないもの（比較例）を試料として作成し、三刺激値を測定した。いずれの試料においてもガラスの厚みは10mm、＊

4

＊酸化鉄の含有量は0．038%である。三刺激値は、明度Yが85%以上、主波長λdが565～575nm、刺激純度Peが1．5%以下の範囲の値となれば、ほぼ良好な無色透明性を有すると判断できるが、主波長については568～572nmの範囲となることが最も好ましい。消色剤として酸化エルビウムを添加した実施例は、いずれも三刺激値がこの最も好ましい範囲にあり、良好な無色透明性を有すると判断できる。また、視覚検査においても、いずれの実施例も比較例に対して無色透明性が向上しており、良好な無色透明ガラスとなっていることが確認された。

【表2】

ガラス厚み：10mm

| 酸化セリウム添加率 | 酸化エルビウム添加率（%） | 三刺激値 | | |
|---|---|---|---|---|
| | | 明度Y% | 主波長λd | 刺激純度Pe |
| 0．3 % | 添加せず | 89．5 | 536．8 | 0．3 |
| | 0．07 | 88．6 | 569．2 | 0．1 |
| 0．4 % | 添加せず | 89．7 | 564．5 | 0．7 |
| | 0．03 | 89．4 | 570．9 | 0．6 |
| 0．5 % | 添加せず | 89．7 | 567．1 | 0．9 |
| | 0．02 | 89．5 | 570．5 | 0．8 |

【0011】

【発明の効果】本発明は、酸化セリウムを添加することで紫外線を吸収し、消色剤として酸化エルビウムを用い※

※たので、安価かつ容易に無色透明性の高いガラスを得ることができる。

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Field of the Invention] Especially this invention is used as a glass bottle, and relates to suitable ultraviolet absorption transparent and colorless glass.
[0002]
[Description of the Prior Art] In the glass bottle, in order to prevent deterioration of contents, ultraviolet rays are absorbed, and what moreover has the transparent and colorless nature which can check the situation of contents to accuracy is desired. Conventionally, as for the glass of such an application, JP,45-17794,B, JP,5-354,B, etc. are ******(ed). The former thing will amend to ** which becomes close to colorlessness by adding the neodium oxide which is a decolorizing agent about the color which tells soda lime glass that cerium oxide adds neodium oxide 0.05 to 0.3% of the weight 0.2 to 0.5% of the weight, absorbs ultraviolet rays by adding cerium oxide, and wears the yellow taste by it. The latter thing is the bottle of the soda lime glass which maximum length of a container was set [ glass ] to 250mm or less, and made 0.04 - 0.1% of cerium oxide, and 0.065% or less of iron oxide contain by weight %. While stopping the content of the iron oxide which ultraviolet rays are too absorbed [ iron oxide ] by adding cerium oxide, and makes the yellow taste promote, it will suppress that glass is visible to yellow with restricting the length between couplings of a bottle as much as possible.
[0003]
[Problem(s) to be Solved by the Invention] Although the thing of the former of the above-mentioned conventional technique is adding the neodium oxide which attaches a purple-blue color, and the yellow of cerium oxide or yellowish green tends to be erased and it is going to bring close to colorlessness, if the daily dose added to the top where a neodium oxide is expensive is difficult and there are, glass will present yellow or yellowish green, and when many [ too ], the technical problem that blue will be presented occurs. [ too few ]
[0004] The thing of the latter of the above-mentioned conventional technique cannot make a large-sized bottle upwards, since there are few additions of a cerium, it will not be able to expect sufficient ultraviolet absorption effectiveness, and since the yellow taste by the cerium oxide cannot be removed, the color of glass will not be able to be made into colorlessness after all, but it will become glass which wore the yellow taste.
[0005] This invention solves such a technical problem, is more cheap and can obtain the ultraviolet absorption transparent and colorless glass easier more near colorlessness.
[0006]
[Means for Solving the Problem] This invention is soda lime glass which contains 0.3 - 0.6% of cerium oxide, and 0.05% or less of ferrous oxide by weight %, and is ultraviolet absorption transparent and colorless glass characterized by adding 0.02 - 0.07% of oxidization erbiums as a decolorizing agent.
[0007] In this invention, the ultraviolet absorption effectiveness is acquired by adding cerium oxide. If too few, an ultraviolet absorption operation is weak, and if there are too many additions of cerium oxide, glass cannot color them strongly, they cannot be made transparent and colorless, but 0.3 - 0.6% of

amount has the good balance of both elements, and is suitable for them. The relation between the rate of addition of cerium oxide and the rate of ultraviolet absorption is shown in a table 1. The rate of ultraviolet absorption was defined as the average absorption coefficient in the applicable wavelength range, and this table computed it. That is, the permeability in every 10nm is subtracted from 100, and average is calculated. Thus, if the addition of cerium oxide is increased, the rate of ultraviolet absorption will improve. 0.3 - 0.6%, then the rate of practical ultraviolet absorption can be obtained. In addition, the thickness of the glass in a table 1 is 3mm.

[A table 1]

ガラス厚み：3㎜　単位：%

| 波長範囲 / 酸化セリウム添加率 | 310 ～ 350nm | 360 ～ 400nm | 310 ～ 400nm |
|---|---|---|---|
| 0 (通常フリント) | 51.68 | 11.31 | 31.49 |
| 0.3% | 91.05 | 18.14 | 54.59 |
| 0.4% | 92.60 | 21.11 | 56.85 |
| 0.6% | 93.93 | 24.28 | 59.10 |

[0008] By adding cerium oxide, the iron which exists as an impurity in glass is oxidized. Therefore, the green stain of divalent iron ion decreases and the yellow of trivalent iron ion increases. Thereby, Lightness Y becomes large, dominant-wavelength lambdad is shifted to a long wavelength side, and the yellow taste cuts [ the color of glass ] it. By stopping the content of the iron oxide which is an impurity to 0.05% or less, the yellow of glass thru/or yellow-green coloring are controlled to the minimum. In addition, stopping the content of an iron oxide to 0.05% or less is being able to make easily for this contractor.

[0009] Glass cannot be made into colorlessness only by stopping the content of an iron oxide. Then, in this invention, 0.02 - 0.07% of oxidization erbiums is added as a decolorizing agent. The color which the yellow taste cut with cerium oxide is amended in [ of an oxidization erbium / light ], and becomes close to colorlessness. Coloring of an oxidization erbium is extremely stable, cannot be easily influenced [ change of an ambient atmosphere, or ] of an oxidizer like cerium oxide, and can acquire desired effectiveness easily.

[0010]

[Example] The example of this invention is shown in a table 2. What does not add cerium oxide with 0.3%, 0.4%, or the thing (example) that added 0.6% and added the decolorizing agent about each (example of a comparison) was created as a sample, and tristimulus values were measured. Also in which sample, the content of 10mm and an iron oxide of the thickness of glass is 0.038%. Although Lightness Y can judge that tristimulus values have almost good transparent and colorless nature if dominant-wavelength lambdad is served as to 565-575nm and excitation purity Pe serves as a value of 1.5% or less of range 85% or more, about the dominant wavelength, it is most desirable to become the range of 568-572nm. Each example which added the oxidization erbium as a decolorizing agent has tristimulus values in this most desirable range, and it can be judged that it has good transparent and colorless nature. Moreover, also in the sight-check, it was checked that transparent and colorless nature of any example is improving to the example of a comparison, and it serves as good transparent and colorless glass.

[A table 2]

ガラス厚み：10mm

| 酸化セリウム添加率 | 酸化エルビウム添加率（%） | 三刺激値 | | |
|---|---|---|---|---|
| | | 明度Y% | 主波長λd | 刺激純度Pe |
| 0.3 % | 添加せず | 89.5 | 536.8 | 0.3 |
| | 0.07 | 88.6 | 569.2 | 0.1 |
| 0.4 % | 添加せず | 89.7 | 564.5 | 0.7 |
| | 0.03 | 89.4 | 570.9 | 0.6 |
| 0.5 % | 添加せず | 89.7 | 567.1 | 0.9 |
| | 0.02 | 89.5 | 570.5 | 0.8 |

[0011]
[Effect of the Invention] Since this invention absorbed ultraviolet rays by adding cerium oxide and the oxidization erbium was used for it as a decolorizing agent, it can obtain the high glass of transparent and colorless nature cheaply and easily.

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PRIOR ART

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[Description of the Prior Art] In the glass bottle, in order to prevent deterioration of contents, ultraviolet rays are absorbed, and what moreover has the transparent and colorless nature which can check the situation of contents to accuracy is desired. Conventionally, as for the glass of such an application, JP,45-17794,B, JP,5-354,B, etc. are ******(ed). The former thing will amend to ** which becomes close to colorlessness by adding the neodium oxide which is a decolorizing agent about the color which tells soda lime glass that cerium oxide adds neodium oxide 0.05 to 0.3% of the weight 0.2 to 0.5% of the weight, absorbs ultraviolet rays by adding cerium oxide, and wears the yellow taste by it. The latter thing is the bottle of the soda lime glass which maximum length of a container was set [ glass ] to 250mm or less, and made 0.04 - 0.1% of cerium oxide, and 0.065% or less of iron oxide contain by weight %. While stopping the content of the iron oxide which ultraviolet rays are too absorbed [ iron oxide ] by adding cerium oxide, and makes the yellow taste promote, it will suppress that glass is visible to yellow with restricting the length between couplings of a bottle as much as possible.

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MEANS

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[Means for Solving the Problem] This invention is soda lime glass which contains 0.3 - 0.6% of cerium oxide, and 0.05% or less of ferrous oxide by weight %, and is ultraviolet absorption transparent and colorless glass characterized by adding 0.02 - 0.07% of oxidization erbiums as a decolorizing agent.
[0007] In this invention, the ultraviolet absorption effectiveness is acquired by adding cerium oxide. If too few, an ultraviolet absorption operation is weak, and if there are too many additions of cerium oxide, glass cannot color them strongly, they cannot be made transparent and colorless, but 0.3 - 0.6% of amount has the good balance of both elements, and is suitable for them. The relation between the rate of addition of cerium oxide and the rate of ultraviolet absorption is shown in a table 1. The rate of ultraviolet absorption was defined as the average absorption coefficient in the applicable wavelength range, and this table computed it. That is, the permeability in every 10nm is subtracted from 100, and average is calculated. Thus, if the addition of cerium oxide is increased, the rate of ultraviolet absorption will improve. 0.3 - 0.6%, then the rate of practical ultraviolet absorption can be obtained. In addition, the thickness of the glass in a table 1 is 3mm.
[A table 1]

ガラス厚み：3㎜　単位：%

| 波長範囲 / 酸化セリウム添加率 | 310 ～ 350nm | 360 ～ 400nm | 310 ～ 400nm |
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effectiveness easily.

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